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(54) Polymerization processes and resin particles formed thereby

(57) A process for the preparation of resin particles comprising: heating a mixture comprised of a free radical initiator compound, at least one stable free radical compound, at least one free radical polymerizable monomer compound, and at least one free radical polymerizable crosslinking compound; and cooling the mixture, wherein the resulting product resin particles are crosslinked and are comprised of polymerized monomers and at least one crosslinking compound, and wherein the particles have a narrow particle size distribution, a narrow pore size distribution, and a high monomer to polymer conversion.

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Description

The present invention is generally directed to processes for the preparation of crosslinked thermoplastic or thermoset resin particles.

Of the known polymerization processes a preferred way to crosslink polymers or copolymers is by free radical processes. Conventional free radical polymerization processes that are used to polymerize monomers in general, and functionalized monomers in particular, inherently give broad polydispersity resin products or require that sophisticated processing conditions and materials handling protocols be employed. The use and availability of crosslinked resins having controlled particle size and operator selectable particle composition in industrial applications is limited because known free radical polymerization processes are generally difficult to control and produce, for example, insoluble polymer gels, even if the crosslinking is accomplished in a separate post polymerization step. Consequently such crosslinking and polymerization processes are generally limited in their industrial utility. Furthermore, the extent to which various functional groups can be directly incorporated into the crosslinked polymer is limited because of physical limitations imposed on conventional free radical polymerization reactions, for example, the preparation of sulfonated polystyrene cross linked ion-exchange particles.

Accordingly, there exists a need for improved processes for producing crosslinked polymers having operator controllable or selectable crosslink density, particle size range, pore size distribution properties and functional group content and further, general processes which can be easily modified to selectively afford a wide variety of different crosslinked polymer product types which are tolerant of a wide variety of functional groups with the aforementioned properties, crosslink density, particle size, pore size distribution properties and functional group content.

In U.S. Patent No. 5,322,912, there is disclosed free radical polymerization processes for the preparation of a thermoplastic resin or resins comprising: heating from about 100 to about 160°C a mixture comprised of a free radical initiator, a stable free radical agent, and at least one polymerizable monomer compound to form the thermoplastic resin or resins with a high monomer to polymer conversion and a narrow polydispersity. A broad spectrum of free radical reactive monomers are suitable for use in the highly versatile polymerization process. While a variety of homopolymers and copolymers, including block and multiblock copolymers, could be prepared with high conversions and narrow polydispersities, no mention was made or suggested to include a crosslinking agent in the polymerization process to prepare crosslinked polymer resins and particles thereof with the aforementioned desirable resin and particle properties.

It is an object, in embodiments, of the present invention to overcome deficiencies of prior art preparative polymerization processes for crosslinked and the like polymeric structures, and to provide polymerization processes with improved efficiency, improved flexibility, and improved operational economies.

According to one aspect of the present invention, there is provided a process for the preparation of resin particles comprising: heating a mixture comprised of a free radical initiator compound, at least one stable free radical compound, at least one free radical polymerizable monomer compound, and at least one free radical polymerizable crosslinking compound; and cooling the mixture.

The free radical polymerization process of the present invention may be used to prepare a variety of crosslinked polymeric materials with well defined and controllable, particle size, particle size distribution, pore size, pore size distribution, and functional group bulk or surface density or distribution.

A "crosslinking compound or agent" or "crosslinker" as used herein refer to those compounds which are capable of forming a crosslink between two polymeric chain segments. The crosslink can, in embodiments, occur or be formed on a single polymer chain but predominantly occurs between two or more different polymeric chains. A "crosslink" refers, in embodiments, to the corresponding polymeric structural element resulting polymerization of one or more of the aforementioned crosslinking agents or compounds. In embodiments of the present invention, a crosslinking agent is capable of producing a crosslink and enables one or more polymer chains to be covalently attached, bridged, or linked. An exemplary free radical polymerizable crosslinking compound contains at least two non adjacent free radical polymerizable double bonds.

Suitable crosslinking agents can be, but are not limited to the general formula

$$CR^1{}_2 = CR^1 - R - CR^1 = CR^1{}_2$$

wherein the crosslinking compounds contains at least two unconjugated free radical polymerizable double bonds, R is a group which separates the two double bonds and can contain such groups as alkyl, alkylene, alkylaryl, and cycloalkyl substituents with from 1 to about 25 carbon atoms, and combinations with various suitable heteroatoms including oxygen, nitrogen, sulfur, phosphorous, and the like atoms, and R^1 groups are independently selected from hydrogen, and carbon containing substituents with from 1 to about 25 carbon atoms.

Suitable free radical polymerizable crosslinking compound include but not limited to vinylstyryl compounds, divi-

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nylstyryl compounds, divinylacrylate compounds, divinyl alkylacrylate compounds, divinylacrylamide compounds, di (N-vinyl) compounds, unconjugated diene compounds, unconjugated diallyl compounds, and mixtures thereof. In embodiments, a preferred crosslinking compound is divinyl benzene. In embodiments, from 1 to about 10 crosslinking compounds selected. In other embodiments, from 2 to about 10 crosslinking compounds selected, for example, when particle having graduated, that is for example, large outer pore sizes going to progressively smaller pore sizes as the center of the particle is approached.

In embodiments of the present invention, the crosslinking compound can be added to the polymerization reaction mixture prior to heating with the other polymerization reactants. In other embodiments, the crosslinking agent is added to the reaction mixture only after a period of time has elapsed where the initial polymerization reaction mixture, in the absence of the crosslinking agent, has been heated, and wherein, generally lower crosslinking densities and larger pore sizes can be achieved. In still other embodiments of the present invention, the crosslinking agent can be added to the heated reaction mixture in regular or variable increments and in various amounts wherein a crosslinked polymer with intermediate, with respect to the abovementioned addition schemes, particle pore properties and particle sizes result.

In still other embodiments, by accomplishing a polymerization reaction using progressively less crosslinking agent, it is possible to obtain particles with gradient pore sizes wherein, for example, the surface or external pores sizes of the particle are relatively large and the pore sizes become progressively smaller as the center of the particle is approached. Particulate pore properties prepared in this manner can be particularly effective and selective as catalyst materials and molecular sieve materials.

In embodiments, the present invention provides efficient and easily controlled processes for preparing thermoplastic or thermoset resins and particulates thereof comprising: heating a mixture comprising a free radical initiator compound, at least one a stable free radical compound, at least one free radical polymerizable monomer, and at least one free radical polymerizable crosslinking compound; and cooling the mixture, wherein the resulting product is comprised of crosslinked thermoplastic or thermoset resin particles, wherein the degree or extent of crosslinking is apparently dependent upon the amount of crosslinking agent used and the extent to which the crosslinking reaction is completed, comprised of polymerized monomers and crosslinking compounds, wherein the particles can have a narrow pore size distribution, if desired. Although not wanting to be limited by theory, apparent controlling factors for particle size are: the crosslinker mole percent relative to the other reactive components; the reaction time; and the initiator concentration. The lower the crosslinker mole percent or the longer the reaction time, the larger the resulting particle size. The higher the free radical initiator concentration the smaller the resulting particle size. The higher the crosslinker mole percent, the smaller the average pore size.

The above simultaneous and sequential polymerization and crosslinking processes can be repeated one or more times, with or without the cooling step between subsequent addition of additional reactants. Thus, the cooling is optional with the exception of when it is desired to isolate a stable polymer

In an exemplary embodiments, there can be selected as starting materials for use in processes of the present invention, a styrene sulfonate compound, such as a sodium salt, as the ionizable polymerizable monomer and a styrene compound as the nonionizable polymerizable monomer, and divinyl benzene as the crosslinking compound, and wherein there results a crosslinked polymeric particulate product with a sulfonate bulk and surface density which substantially proportional to the amount of styrene sulfonate employed.

In embodiments of the present invention, there are provided processes for preparing high capacity and high efficiency ion exchange materials, which are believed to be enabled by the present process by way of the ability to selectively introduce high concentrations of ionic functionality into the polymer during polymer chain formation. Ion exchange capacities of from 5 to 95 percent are believed to readily attainable and as illustrated herein.

In embodiments, resin particulate pore sizes can range on average from about 10 nanometers for low crosslinker mole ratio situations to from about 1,000 nanometers for high crosslinker mole ratio situations.

In embodiments of the present invention, a single crosslinking compound or from 2 to about 10 free crosslinking compounds can be included in the reaction mixture prior to heating or added sequentially during the course of the heating of the polymerization reaction mixture, for example, in the preparation of crosslinked polymers which can be structurally and or physically differentiated by the crosslinking compounds selected and the time sequence used for the addition of different crosslinking compounds to the polymerization mixture. In other embodiments, the crosslinker can be added after substantially all the monomer has been consumed in the normal course of a stable free radical agent mediated polymerization step. Thus, the type of crosslinker compound selected and the crosslinker addition time sequence executed can be used to markedly influence and control structural aspects of the polymer and the product particles, and provide readily identifiable structural components and a distinctive indication of when those structural components were formed in the polymerization sequence.

In other embodiments of the present invention, highly crosslinked polymer products with very small and uniform pore size and size distribution can be obtained by employing large amounts of crosslinking compound relative to the free radical polymerizable monomer, and although not wanting to be limited by theory it appears that as the monomer

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concentration decreases relative to the crosslinker compound concentration, the aforementioned pore size and pore size distribution relation becomes increasingly smaller.

Polymerizable monomers suitable for use in the present invention, in embodiments, include any free radical reactive unsaturated compounds such as styrene compounds; unsaturated hydrocarbon compounds; conjugated diene compounds; acrylate esters and alkyl acrylate esters with from 5 to 25 carbon atoms; N-vinyl acetates; amine, carboxyl, aldehyde, alkyl, cyano, and hydroxyl substituted acrylic acids and acrylic acid esters having from 2 to about 20 carbon atoms; acrylamide; methacrylamide; acrylic acid; methacrylic acid; acrolein; dimethylaminoacrylate; hydroxy alkyl, and amino alkyl acrylates of the formula CH2=C(-R1)-(C=Z)-R2 where R1 is hydrogen, R2 is selected from the group consisting of $-OR_1$ and $-NR_1R_2$ where R_1 and R_2 have from 1 to about 10 carbon atoms, and where Z is selected from the group consisting of oxygen and sulfur atoms; and mixtures thereof. In embodiments, from 1 to about 10 different free radical polymerizable monomers can be selected and simultaneously polymerized in any given monomer addition polymerization step. In other embodiments of the present invention, a single monomer or from 2 to about 10 free radical polymerizable monomers can be included in the reaction mixture prior to heating or added sequentially during the course of the heating of the polymerization reaction mixture, for example, in the preparation of block or multiblock copolymers.

The heating is preferably accomplished in from about 30 minutes to about 60 hours at a temperature of from about 70 to about 175°C.

The cooling of the polymerization mixture is preferably accomplished below about 100 °C, preferably below about 80 °C, and more preferably below about 40°C to about 60°C temporarily or permanently suspend the monomer addition polymerization process.

In embodiments of the present invention, it is envisioned that the resulting crosslinked resin particles can be combined with at least one additional additive or formulation component, such as a colorant, a magnetic component, a charge control additive, a surfactant, an emulsifier, and a pigment dispersant, a second non crosslinked resin, to form a mixture, and wherein the mixture is melt blended to form a mixture suitable for use as a toner. The combination with other additives can be accomplished prior to, during, or subsequent to the heating step. In embodiments, the resulting crosslinked resin particles can be combined with, for example, an inorganic element, an inorganic oxide compound, and mixtures thereof for the purpose of preparing filled resins which are useful as, for example, magnetic toners.

In other embodiments of the present invention, it is envisioned that the initial reaction mixture can be combined at least one other additive or formulation component, such as a colorant, a charge control additive, a surfactant, an emulsifier, a pigment dispersant, and mixtures thereof, prior to heating, to form a second mixture comprised of particles suitable for use as a toner when the mixture is subsequently polymerized with heating, irradiation, and equivalent means for effecting stable free radical mediated type polymerizations.

In other embodiments of the present, it is possible to copolymerize mixtures of mono- and or difunctional free radical reactive monomers, such as olefins and conjugated dienes, and crosslinking compounds with mono- or multifunctional branching agent monomers to produce various crosslinked and branched copolymer architectures or copolymeric segments structures which contain both monomer types. Some advantages of the aforedescribed process variant include the ability to prepare highly crosslinked and branched copolymeric materials, and the ability to eliminate additional, separate, or unnecessary polymerization, crosslinking, and chain branching steps.

In embodiments of the present invention, the monomer to polymer conversions typically range of from about 10 to about 100 percent depending upon polymerization/crosslinking conditions selected; the extent to which the steps in the crosslinking are completed; and the number of times the concurrent polymerization and crosslinking sequence is successively repeated.

The processes can be operated as batch, semi-continuous or continuous processes. The processes can be carried out in solution, bulk, suspension, emulsion, phase transfer, and extrusion reaction conditions. The processes of the present invention provide from about 1 to about 99 percent by weight of the reaction mixture prior to polymerization and crosslinking to be a free radical reactive monomer or monomer mixtures. The processes produce polymer products which have operator selectable low, intermediate, or high molecular weight; well defined crosslinking properties; low residual salt content or are salt free; posses thermal and acidic stability; and low toxicity; if desired.

In embodiments, the present invention overcomes many of the problems and disadvantages of the aforementioned related art crosslinking polymerization processes by forming in situ, high functional group content crosslinked polymeric resins and wherein high conversion from monomer to polymer is achieved, for example, as illustrated herein.

The stable free radical agent, in embodiments of the present invention, is comprised of a compound with a sterically hindered atom bearing a stable free radical, selected from the group consisting of sterically hindered nitroxyl compounds, organic hydrazyls, organic verdazyls, pyridinyl compounds, organic aroxyls, aryl alkyls and aryl cycloalkyls in which the unpaired electron is on a carbon atom in the alkyl or cycloalkyl group, and compatible mixtures thereof, and wherein the stable free radical agent is thermally stable, that is the compound itself does not decompose to any extent under the conditions of the present process, and does not react to any appreciable extent with conventional free radical initiator compounds, such as benzoyl peroxide and peroxy radical species derived therefrom upon thermal or photo-

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chemical dissociation of the peroxide.

The stable free radical compound when covalently bound to the polymer product preferably has no unpaired electrons, that is, has no free radical character or free unpaired electrons.

Suitable stable free radical compounds for use in the present are known, and can be prepared prior to mixing with the other polymerization reactants or they may be generated in situ or on an as needed basis. Examples include the non-nitroxyl type stable free radical compounds described in "Free Radicals" Volumes I and II, edited by J.K. Kochi, Wiley-Interscience, New York, 1973, and in U.S. Patent No. 5,530,079.

The stable free radical agent compounds of the present invention may be generated in any suitable fashion from the corresponding non-free radical precursor, for example, thermally, chemical, electrochemically, photolytically, mechanically, and the like methods.

Examples of suitable and preferred stable free radicals are disclosed in U.S. Patent No. 3,600,169.

The monomer or monomers to be polymerized in embodiments can be dissolved in water or aqueous mixtures of polar protic or aprotic organic solvents. The resultant aqueous solution usually contains a suitable water-soluble, free-radical generating initiator such as a peroxide or a persulfate, and the like, as defined herein. The monomer or monomers are used in effective amounts relative to the free radical initiator, and stable free radical agent, as defined hereinafter.

Suitable initiators for the polymerization processes of the present invention are any conventional free radical initiators which have a half-life of at least 1 second at the polymerization temperature. Preferably, the initiator will have a half life of from about 10 second to about 2 hours, more preferably from about 10 seconds to about 10 minutes at the polymerization reaction temperature. These initiators include, but are not limited to oxygen, hydrogen peroxide, certain alkyl hydroperoxides, dialkyl peroxides, peresters, percarbonates, peroxides, persulfates and azo initiators. Specific examples of some suitable initiators include hydrogen peroxide, t-butyl hydroperoxide, di-tertiary butyl peroxide, tertiary-amyl hydroperoxide, potassium persulfate, dibenzoyl peroxide, and methylethyl ketone peroxide. The initiators are normally used in amounts of from about 0.05 percent to about 33 percent based on the weight of total polymerizable monomer. A preferred range is from about 0.5 to about 20 percent by weight of the total polymerizable monomer. In embodiments, the molar ratio of monomer to stable free radical agent to free radical initiator compounds is from about 50:0.2:1.0 to about 20,000:2.5:1.0. Preferred free radical initiators do not react with or degrade the stable free radical compounds with the exception of the aforementioned in situ stable free radical generation resulting from the reaction of the stable free radical precursor compound with a free radical fragment species.

The free radical initiator can be any free radical polymerization initiator capable of initiating a free radical polymerization process of unsaturated monomers and includes peroxide initiators such as benzoyl peroxide, persulfate initiators such as potassium persulfate, azo initiators such as azobisisobutyronitrile, and the like. The initiator concentration employed is, for example, about 0.2 to about 16.0 weight percent of the total weight of monomer to be polymerized and is determined by the desired molecular weight of the resin. As the initiator concentration is decreased relative to the weight or molar equivalents of monomer used, the molecular weight of the resin or elastomer product increases.

Water soluble free radical initiators can be optionally employed and include persulfates; water soluble peroxides and hydroperoxides; more specifically, sodium, potassium and ammonium persulfate; peroxides such as hydrogen peroxide, t-butyl hydroperoxide, cumene hydroperoxide, para-menthane hydroperoxide; and peroxy carbonates.

In other embodiments, the polymerization processes of the present invention can be used to prepare crosslinked block copolymers and multi-block polymers, wherein at least one of the blocks is optionally water soluble thereby providing, for example, a method for preparing crosslinked or networked surface active agents, surfactant materials, and highly surface active particles, having well defined critical micelle concentration (CMC) and hydrophobe-lipophobe balance (HLB) properties.

The present invention describes crosslinked polymers and particles prepared by a stable free radical mediated free radical polymerization process in which control over the primary polymer chain lengths can be exercised if desired. This control provides substantial advantages in various applications such as viscosity modification, matrix strengthening and resin clarity improvement, since these properties depend to a substantial extent on the tertiary structure of the crosslinked polymer.

The present invention provides crosslinked polymer products with a latent thermally reactive or latent functional group on at least one end or terminus of the crosslinked polymer and which latent functional group can be used for further reaction with for example, a free radical reactive small or large molecule for the purpose of isolating and fixing the molecule to, for example, a polymeric matrix.

The polymerization reactions of the present invention can be supplemented with a solvent or cosolvent if desired to help ensure that the reaction mixture or at least the monomer containing portion remains a homogeneous single phase throughout the monomer conversion. Any solvent or cosolvent may be selected so long as the solvent media is effective in providing a solvent system which avoids precipitation or phase separation of the reactants or polymer products until after all the solution polymerization reactions have been completed. Exemplary solvent or cosolvents include aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkyl pyrrolidinones, N-alkyl pyrrolidones, pol-

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yethylene glycols, polypropylene glycols, amides, carboxylic acids and salts thereof, esters, organosulfides, sulfoxides, sulfones, alcohol derivatives, hydroxyether derivatives such as butyl CARBITOL® or CELLOSOLVE®, amino alcohols, ketones, and the like, derivatives thereof, and mixtures thereof. Specific examples include ethylene glycol, propylene glycol, diethylene glycol, glycerine, dipropylene glycol, tetrahydrofuran, and mixtures thereof. When mixtures of water and water soluble or miscible organic liquids are selected as the reaction media, the water to cosolvent weight ratio typically ranges from about 100:0 to about 10:90, and preferably from about 97:3 to about 25:75.

The polymerization reaction rate of the monomers may, in embodiments, be inhibited or accelerated and the reaction time influenced by the addition of minor amounts of a protic acid selected from the group consisting of inorganic acids, such as sulfuric, hydrochloric, and the like, and organic sulfonic and carboxylic acids. Although a definitive trend is presently not well defined, the added acid may have a profound or very little effect on the polymerization rate, depending upon a variety of reaction variables and conditions. Excessive addition of inorganic and organic acid beyond equimolar amounts compared to the stable free radical agent causes the polydispersity of the primary polymer chain to broaden. In embodiments, the protic acid source may be in the form of an effective acid functional group such as carboxylic, sulfonic, phosphonic, and the like groups, contained in either the stable free radical agent or in the free radical initiator compound.

Alternatively, crosslinked block copolymer resins may also be prepared whereby after each desired block has been formed a new monomer or monomers is added, without the addition of more initiator or stable free radical agent, to form a new block wherein each block component is well defined in length and has a narrow molecular weight distribution and having properties depending on the repeated sequence and the monomers chosen for incorporation. Monomers added subsequent to the formation of the first formed crosslinked resin or elastomer may be water soluble or water insoluble. Judicious selection of the water solubility properties of added monomers and the resulting polymeric segment enables convenient synthetic routes to crosslinked block and multiblock copolymers having primary structures or polymer chains with narrow polydispersities that are useful, for example, as surfactants, resin compatibilizers, such as "molecular velcro", geometrically well defined polymeric resin particles which are readily and highly dispersible in water or aqueous vehicles, viscosity modifiers, and emulsifiers.

Additional optional known additives may be used in the polymerization reactions which do not interfere with the objects of the invention and which may provide additional performance enhancements to the resulting crosslinked product, for example, colorants, lubricants, release or transfer agents, surfactants, stabilizers, antifoams, and antioxidants.

Illustrative examples of resins obtained with the invention processes and suitable for toner and developer compositions of the present invention include crosslinked, and mixtures of crosslinked and uncrosslinked polymers, such as styrene acrylates, styrene methacrylates, styrene butadienes, vinyl resins, including homopolymers and copolymers of two or more vinyl monomers; vinyl monomers include styrene, butadiene, and myrcene; vinyl esters like esters of monocarboxylic acids including methyl acrylate, n-octyl acrylate, phenyl acrylate, methyl methacrylate, butyl methacrylate: acrylonitrile, methacrylonitrile, and acrylamide. Preferred toner resins include styrene butadiene copolymers, and mixtures thereof. Other preferred toner resins include styrene/n-butyl acrylate copolymers, PLIOLITES®; suspension polymerized styrene butadienes, reference U.S. Patent 4,558,108.

In toner compositions, the resin particles are present in a sufficient but effective amount, for example from about 70 to about 90 weight percent. Thus, when 1 percent by weight of the charge enhancing additive is present, and 10 percent by weight of pigment or colorant, such as carbon black, is contained therein, about 89 percent by weight of resin is selected. Also, the charge enhancing additive may be coated on the pigment particle. When used as a coating, the charge enhancing additive is present in an amount of from about 0.1 weight percent to about 5 weight percent, and preferably from about 0.3 weight percent to about 1 weight percent.

Numerous well known suitable pigments or dyes can be selected as the colorant for the toner particles including, for example, carbon black like REGAL 330® (tradename), nigrosine dye, aniline blue, magnetite, or mixtures thereof. The pigment, which is preferably carbon black, should be present in a sufficient amount to render the toner composition highly colored. Generally, the pigment particles are present in amounts of from about 1 percent by weight to about 20 percent by weight, and preferably from about 2 to about 10 weight percent based on the total weight of the toner composition; however, lesser or greater amounts of pigment particles can be selected.

When the pigment particles are comprised of magnetites, thereby enabling single component toners in some instances, which magnetites are a mixture of iron oxides ($FeO \cdot Fe_2O_3$) including those commercially available as MAPICO BLACK® (tradename), they are present in the toner composition in an amount of from about 10 percent by weight to about 70 percent by weight, and preferably in an amount of from about 10 percent by weight to about 50 percent by weight. Mixtures of carbon black and magnetite with from about 1 to about 15 weight percent of carbon black, and preferably from about 2 to about 6 weight percent of carbon black, and magnetite, such as MAPICO BLACK® (tradename), in an amount of, for example, from about 5 to about 60, and preferably from about 10 to about 50 weight percent can be selected.

There can also be blended with the toner compositions of the present invention external additive particles including

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flow aid additives, which additives are usually present on the surface thereof. Examples of these additives include colloidal silicas, such as AEROSIL®, metal salts and metal salts of fatty acids inclusive of zinc stearate, aluminum oxides, cerium oxides, and mixtures thereof, which additives are generally present in an amount of from about 0.1 percent by weight to about 5 percent by weight, and preferably in an amount of from about 0.1 percent by weight to about 1 percent by weight. Several of the aforementioned additives are illustrated in U.S. Patents 3,590,000 and 3,800,588, the disclosures of which are totally incorporated herein by reference.

With further respect to the present invention, colloidal silicas, such as AEROSIL®, can be surface treated with the charge additives in an amount of from about 1 to about 30 weight percent and preferably 10 weight percent followed by the addition thereof to the toner in an amount of from 0.1 to 10 and preferably 0.1 to 1 weight percent.

Also, there can be included in the toner compositions low molecular weight waxes, such as polypropylenes and polyethylenes commercially available from Allied Chemical and Petrolite Corporation, EPOLENE N-15® (tradename), commercially available from Eastman Chemical Products, Inc., VISCOL 550-P® (tradename), a low weight average molecular weight polypropylene available from Sanyo Kasei K.K., and similar materials. The commercially available polyethylenes selected have a molecular weight of from about 1,000 to about 1,500, while the commercially available polypropylenes utilized for the toner compositions are believed to have a molecular weight of from about 4,000 to about 5,000. Many of the polyethylene and polypropylene compositions useful in the present invention are illustrated in British Patent No. 1,442,835.

The low molecular weight wax materials are optionally present in the toner composition or the polymer resin beads of the present invention in various amounts, however, generally these waxes are present in the toner composition in an amount of from about 1 percent by weight to about 15 percent by weight, and preferably in an amount of from about 2 percent by weight to about 10 percent by weight and may in embodiments function as fuser roll release agents.

Encompassed within the scope of the present invention are colored toner and developer compositions comprised of toner resin particles, carrier particles, the charge enhancing additives illustrated herein, and as pigments or colorants red, blue, green, brown, magenta, cyan and/or yellow particles, as well as mixtures thereof. More specifically, with regard to the generation of color images utilizing a developer composition with charge enhancing additives, illustrative examples of magenta materials that may be selected as pigments include, for example, 2,9-dimethyl-substituted quinacridone and anthraquinone dye identified in the Color Index as CI 60710, and CI Dispersed Red 15. Illustrative examples of cyan materials that may be used as pigments include copper tetra-4-(octadecyl sulfonamido) phthalocyanine and Special Blue X-2137; while illustrative examples of yellow pigments that may be selected are diarylide yellow 3,3-dichlorobenzidene acetoacetanilides, and Permanent Yellow FGL. The aforementioned pigments are incorporated into the toner composition in various suitable effective amounts providing the objectives of the present invention are achieved. In one embodiment, these colored pigment particles are present in the toner composition in an amount of from about 2 percent by weight to about 15 percent by weight calculated on the weight of the toner resin particles.

For the formulation of developer compositions, there are mixed with the toner particles carrier components, particularly those that are capable of triboelectrically assuming an opposite polarity to that of the toner composition. Accordingly, the carrier particles are selected to be of a negative polarity enabling the toner particles, which are positively charged, to adhere to and surround the carrier particles. Illustrative examples of carrier particles include iron powder, steel, nickel, iron, ferrites, including copper zinc ferrites, and the like. Additionally, there can be selected as carrier particles nickel berry carriers as illustrated in U.S. Patent 3,847,604. The selected carrier particles can be used with or without a coating, the coating generally containing terpolymers of styrene, methylmethacrylate, and a silane, such as triethoxy silane, reference U.S. Patent 3,526,533, U.S. Patent 4,937,166, and U.S. Patent 4,935,326, including for example KYNAR® and polymethylmethacrylate mixtures (40/60). Coating weights can vary as indicated herein; generally, however, from about 0.3 to about 2, and preferably from about 0.5 to about 1.5 weight percent coating weight is selected.

Furthermore, the diameter of the carrier particles, preferably spherical in shape, is generally from about 50 microns to about 1,000 microns, and in embodiments about 175 microns thereby permitting them to possess sufficient density and inertia to avoid adherence to the electrostatic images during the development process. The carrier component can be mixed with the toner composition in various suitable combinations, however, best results are obtained when about 1 to 5 parts per toner to about 10 parts to about 200 parts by weight of carrier are selected.

The toner composition of the present invention can be prepared by a number of known methods as indicated herein including extrusion melt blending the toner resin particles, pigment particles or colorants, and a charge enhancing additive, followed by mechanical attrition. Other methods include those well known in the art such as spray drying, melt dispersion, emulsion aggregation, and extrusion processing. Also, as indicated herein the toner composition without the charge enhancing additive in the bulk toner can be prepared, followed by the addition of charge additive surface treated colloidal silicas.

The toner and developer compositions may be selected for use in electrostatographic imaging apparatuses containing therein conventional photoreceptors providing that they are capable of being charged positively or negatively. Thus, the toner and developer compositions can be used with layered photoreceptors that are capable of being charged

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negatively, such as those described in U.S. Patent 4,265,990. Illustrative examples of inorganic photoreceptors that may be selected for imaging and printing processes include selenium; selenium alloys, such as selenium arsenic, selenium tellurium and the like; halogen doped selenium substances; and halogen doped selenium alloys.

The toner compositions are usually jetted and classified subsequent to preparation to enable toner particles with a preferred average diameter of from about 5 to about 25 micrometers (5 to about 25 microns), and more preferably from about 8 to about 12 micrometers (8 to about 12 microns). Also, the toner compositions preferably possess a triboelectric charge of from about 0.1 to about 2 femtocoulombs per micron as determined by the known charge spectrograph. Admix time for toners are preferably from about 5 seconds to 1 minute, and more specifically from about 5 to about 15 seconds as determined by the known charge spectrograph.

Also, the toner compositions prepared from resins of the present invention possess desirable narrow charge distributions, optimal charging triboelectric values, preferably of from 10 to about 40, and more preferably from about 10 to about 35 microcoulombs per gram as determined by the known Faraday Cage methods with from about 0.1 to about 5 weight percent in one embodiment of the charge enhancing additive; and rapid admix charging times as determined in the charge spectrograph of less than 15 seconds, and more preferably in some embodiments from about 1 to about 14 seconds.

EXAMPLE I

Preparation of Crosslinked Poly(styrene sulfonate-sodium salt) 1:1 molar ratio of SS-Na and DVB. To a round bottom flask was added styrenesulfonate-sodium salt (SS-Na, 10 g, 0.0487 mole), divinylbenzene (DVB, 6.34 g, 0.0487 mole), and TEMPO (0.91 g, 0.00583 mole). To this was added ethylene glycol (24 mL) and water (16 mL) and heated to 80°C. Then a redox initiator system, potassium persulfate (0.877 g, 0.00324 mole) and sodium bisulfite (0.44 g), was added. After one half hour, the heterogeneous solution was heated to reflux. After 7 hours, the reaction was cooled and precipitated into a solution of methanol/acetone (220 mL 1:1 ratio). The white powder was isolated and dried to yield 12.2 g (66%) of product.

EXAMPLE II

Preparation of Crosslinked Poly(styrene sulfonate-sodium salt) 1:0.5 molar ratio of SS-Na and DVB. To a round bottom flask was added styrenesulfonate-sodium salt (SS-Na, 10 g, 0.0487 mole), divinylbenzene (DVB, 3.17 g, 0.02435 mole), and TEMPO (0.688 g. 0.00438 mole). To this was added ethylene glycol (24 mL) and water (16 mL) and heated to 80°C. Then a redox initiator system, potassium persulfate (0.656 g, 0.00243 mole) and sodium bisulfite (0.376 g), was added. After one half hour, the heterogeneous solution was heated to reflux. After 7 hours, the reaction was cooled and precipitated into a solution of methanol/acetone (200 mL 1:1 ratio). The white powder was isolated and dried to yield 9.2 g (62%) of product.

EXAMPLE III

Preparation of Crosslinked Poly(styrene sulfonate-sodium salt) 1:0.33 molar ratio of SS-Na and DVB. To a round bottom flask was added styrenesulfonate-sodium salt (SS-Na 10 g, 0.0487 mole), divinylbenzene (DVB, 2.1 g, 0.0162 mole) and TEMPO (0.606 g, 0.00389 mole). To this was added ethylene glycol (24 mL) and water (16 mL) and heated to 80°C. A redox initiator system, potassium persulfate (0.584 g, 0.00216 mole) and sodium bisulfite (0.292 g), was added. After 40 minutes, the heterogeneous solution was heated to reflux. After 7 hours, the reaction was cooled and precipitated into a solution of methanol/acetone (200 mL, 1:1 ratio). The white powder was isolated and dried to yield 10.1 g (74%) of product.

EXAMPLE IV

Preparation of Crosslinked Poly(styrene sulfonate-sodium salt) 1:0.16 molar ratio of SS-Na and DVB. To a round bottom flask was added styrenesulfonate-sodium salt (SS-Na, 10 g, 0.0487 mole), divinylbenzene (DVB, 1.05 g, 0.0081 mole), and TEMPO (0.53 g, 0.00341 mole). To this was added ethylene glycol (24 mL) and water (16 mL) and heated to 80°C. Then a redox initiator system, potassium persulfate (0.51 g, 0.00189 mole) and sodium bisulfite (0.25 g), was added. After 40 minutes, the heterogeneous solution was heated to reflux. After 7 hours, the reaction was cooled and precipitated into a solution of methanol/acetone (200 mL, 1:1 ratio). The white powder was isolated and dried to yield 5.0 g (41%) of product.

The four products from the respective Examples I-IV were particulate powders and were free flowing. The free flowing property suggests that there was no gel formation in the reaction mixtures. The isolated particulate solids were dispersed in water and the particle sizes measured on a NICOMP submicron particle sizer (Model 370) or a Brookhaven

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Instruments BI-DCP disk centrifuge particle sizer. The particle sizes are reported in volume weighted distribution using the Brookhaven Instruments BI-DCP disk centrifuge particle sizer. The maximum in the particle distribution, that is, maximum particle size occurrence in the particle size distribution is given the column labeled "particle size". The distribution range of particle sizes, from the smallest to largest particle size, is given in the column labeled "Distr. Range".

Table 1.

Example	SS-Na:DVB	Particle Size (nm)	Distr. Range
I	1:1	350	210 nm-1 micrometer
II	1:0.5	600	450 nm-1 micrometer
III	1:0.33	700	420 nm-1.4 micrometer
IV	1:0.16	840	630 nm-1.5 micrometer

EXAMPLE V

Preparation of Crosslinked Copoly(styrene-styrene sulfonate-sodium salt) 1.0:1.0:0.5 molar ratio of St:SS-Na:DVB To a round bottom flask is added styrenesulfonate-sodium salt (SS-Na, 10 g, 0.0487 mole), styrene (5.06g, 0.0487 mole), divinylbenzene (DVB, 3.17 g, 0.02435 mole), and TEMPO (0.53 g, 0.00341 mole). To this is added ethylene glycol (24 mL) and water (16 mL) and heated to 80°C. Then a redox initiator system, potassium persulfate (0.51 g, 0.00189 mole) and sodium bisulfite (0.25 g), is added. After 40 minutes, the heterogeneous solution is heated to reflux. After 7 hours, the reaction is cooled and precipitated into a solution of methanol/acetone (200 mL, 1:1 ratio).

EXAMPLE VI

Preparation of Crosslinked Copoly(butylacrylate-styrene sulfonate-sodium salt) 1.0:0.5 molar ratio of SS-Na:DVB To a round bottom flask is added styrenesulfonate-sodium salt (SS-Na, 10 g, 0.0487 mole), butylacrylate (6.24, 0.0487 mole), divinylbenzene (DVB, 3.17 g, 0.02435 mole), and TEMPO (0.53 g, 0.00341 mole). To this is added ethylene glycol (24 mL) and water (16 mL) and heated to 80°C. Then a redox initiator system, potassium persulfate (0.51 g, 0.00189 mole) and sodium bisulfite (0.25 g), is added. After 40 minutes, the heterogeneous solution is heated to reflux. After 7 hours, the reaction is cooled and precipitated into a solution of methanol/acetone (200 mL, 1:1 ratio).

EXAMPLE VII

Preparation of Crosslinked polystyrene 1.0:0.03 molar ratio of styrene:DVB To a round bottom flask is added styrenes (10 g, 0.096 mole), divinylbenzene (DVB, 0.375 g, 0.00288 mole), and TEMPO (0.53 g, 0.00341 mole). To this is added ethylene glycol (24 mL) and water (16 mL) and heated to 80°C. Then a redox initiator system, potassium persulfate (0.51 g, 0.00189 mole) and sodium bisulfite (0.25 g), is added. After 40 minutes, the heterogeneous solution is heated to reflux. After 7 hours, the reaction is cooled and precipitated into a solution of methanol/acetone (200 mL, 1:1 ratio).

EXAMPLE VIII

Magnetic Toner Preparation and Evaluation The polymer resin (74 weight percent of the total mixture) obtained by the stable free radical polymerization processes in Example I may be melt extruded with 10 weight percent of REGAL 330® carbon black and 16 weight percent of MAPICO BLACK® magnetite at 120°C, and the extrudate pulverized in a Waring blender and jetted to 8 micron number average sized particles. A positively charging magnetic toner may be prepared by surface treating the jetted toner (2 grams) with 0.12 gram of a 1:1 weight ratio of AEROSIL R972® (Degussa) and TP-302 a naphthalene sulfonate and quaternary ammonium salt (Nachem/Hodogaya SI) charge control agent. Other toner additives can be optionally added to adjust the magnitude or sign of the charge on the toner particles as desired, reference for example, U.S. Patent No. 4,937,157.

Developer compositions may then be prepared by admixing 3.34 parts by weight of the aforementioned toner composition with 96.66 parts by weight of a carrier comprised of a steel core with a polymer mixture thereover containing 70 percent by weight of KYNAR®, a polyvinylidene fluoride, and 30 percent by weight of polymethyl methacrylate; the coating weight being about 0.9 percent. Cascade development may be used to develop a Xerox Model D photoreceptor using a "negative" target. The light exposure may be set between 5 and 10 seconds and a negative bias used to dark transfer the positive toned images from the photoreceptor to paper.

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Claims

1. A process for the preparation of resin particles comprising:

   heating a mixture comprised of a free radical initiator compound, at least one stable free radical compound, at least one free radical polymerizable monomer compound, and at least one free radical polymerizable crosslinking compound;
   and cooling the mixture.

2. A process in accordance with claim 1 wherein the resulting product resin particles are crosslinked and are comprised of polymerized monomers and at least one crosslinking compound, and wherein the particles have a narrow particle size distribution and a narrow pore size distribution, and a high monomer to polymer conversion.

3. A process in accordance with either of claims 1 or 2, wherein there is selected an ionizable polymerizable monomer and a nonionizable polymerizable monomer in an amount of from about 99:1 to about 1:99 mole percent, and wherein there results a crosslinked polymeric product with an ionic group bulk and surface density which is substantially proportional to the ionizable monomer mole percent present during heating.

4. A process in accordance with claim 3, wherein there is selected a styrene sulfonate compound as the ionizable polymerizable monomer and a nonionizable styrene compound as the nonionizable polymerizable monomer in a mole ratio of from about 100:0 to about 1:99, and a divinyl benzene compound as the crosslinking compound in a mole ratio of from about 0.01:1.0 to about 0.75:1.0 with respect to the polymerizable monomers, and wherein there results a crosslinked polymeric product with a sulfonate bulk and surface density of from about 99.99 mole percent to about 0.99 mole percent.

5. A process in accordance with any of claims 1 to 4, wherein the free radical polymerizable crosslinking compounds selected contains at least two non adjacent free radical polymerizable double bonds.

6. A process in accordance with any of claims 1 to 4, wherein the free radical polymerizable crosslinking compound is selected from the group consisting of vinylstyryl compounds, divinylstyryl compounds, divinylacrylate compounds, divinyl alkylacrylate compounds, divinylacrylamide compounds, di (N-vinyl) compounds, unconjugated diene compounds, unconjugated diallyl compounds, and mixtures thereof.

7. A process in accordance with any of claims 1 to 6, wherein the stable free radical compound is selected from the group consisting of sterically hindered nitroxyl compounds, organic hydrazyls, organic verdazyls, pyridinyl compounds, organic aroxyls, aryl alkyls and aryl cycloalkyls in which the unpaired electron is on a carbon atom in the alkyl or cycloalkyl group, and compatible mixtures thereof.

8. A process in accordance with claim 1 wherein the free radical polymerizable monomer is a reactive unsaturated compound selected from the group consisting of styrene compounds, unsaturated hydrocarbon compounds, conjugated diene compounds, acrylate esters and alkyl acrylate esters with from 5 to 25 carbon atoms, N-vinyl acetates, amine, carboxyl, aldehyde, alkyl, cyano, and hydroxyl substituted acrylic acids and acrylic acid esters having from 2 to about 20 carbon atoms; acrylamide; methacrylamide; acrylic acid; methacrylic acid; acrolein; dimethylaminoacrylate; hydroxy alkyl, and amino alkyl acrylates of the formula CH2=C(-R1)-(C=Z)- R2 where R1 is hydrogen, R2 is selected from the group consisting of $-OR_1$ and $-NR_1R_2$ where R_1 and R_2 have from 1 to about 10 carbon atoms, and where Z is selected from the group consisting of oxygen and sulfur atoms; and mixtures thereof.

9. A process in accordance with any of claims 1 to 8, further comprising combining with the mixture prior to or during heating, at least one member selected from the group consisting of a colorant, a magnetic component, a charge control additive, a surfactant, an emulsifier, a pigment dispersant, and mixtures thereof, to form a second mixture comprised of particles suitable for use as a toner.

10. A process in accordance with any of claims 1 to 8, further comprising combining the resulting crosslinked resin particles with at least one member selected from the group consisting of a colorant, a magnetic component, a charge control additive, a surfactant, an emulsifier, a pigment dispersant, and mixtures thereof, to form a mixture, and wherein the mixture is melt blended to form a toner.

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(54) Polymerization processes and resin particles formed thereby

(57) A process for the preparation of resin particles comprising: heating a mixture comprised of a free radical initiator compound, at least one stable free radical compound, at least one free radical polymerizable monomer compound, and at least one free radical polymerizable crosslinking compound; and cooling the mixture, wherein the resulting product resin particles are crosslinked and are comprised of polymerized monomers and at least one crosslinking compound, and wherein the particles have a narrow particle size distribution, a narrow pore size distribution, and a high monomer to polymer conversion.

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	WO 94 11412 A (XEROX) 26 May 1994		C08F4/00 G03G9/087
A	EP 0 135 280 A (COMMONWEALTH SCIENTIFIC AND IND. RESEARCH ORG.) 27 March 1985		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 July 1998	Cauwenberg, C

CATEGORY OF CITED DOCUMENTS

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